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Second Quarterly Progress Report
September, October, November, 1962

to

Aeronautical Systems Division
Wright-Patterson Air Force Base
Ohio

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FACTORS AFFECTING THE COMPATIBILITY OF
LIQUID CESIUM WITH CONTAINMENT METALS

F. Tepper
S. J. Rodgers
J. S. Greer

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ABSTRACT

The analytical phase of the program has been directed toward establishing techniques for oxygen, nitrogen and carbon in cesium. Since the analytical procedures employed for carbon (10 ppm \pm 5 ppm) and nitrogen (2 ppm \pm 2 ppm) in sodium were easily adapted to cesium, the bulk of the effort has been on development of an oxygen analytical technique. Results indicate that the standard amalgamation technique gives consistently low results for oxygen in cesium. Of the other two techniques evaluated, the MSAR sodium amalgam and the butyl bromide techniques, the sodium amalgam technique seems to be most reliable. This technique has been applied to potassium on an in-house sponsored effort to verify the method. ~~No significant differences in values were observed between samples of potassium analyzed via the standard amalgamation technique and the sodium amalgam method.~~

The mechanisms associated with the attack of structural materials by isothermal liquid cesium are being studied. Capsules of Mo-1/2%Ti have been prepared for study of the solution kinetics of this alloy into liquid cesium at 2500°F. Dissimilar metal studies with Haynes-25 and Cb-1%Zr have been initiated. () 

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on
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ANALYTICAL RESULTS

Nitrogen

Nitrogen, as cesium nitride, is determined by a modified Kjeldahl method wherein nitride is converted to ammonia, distilled from a caustic solution, absorbed in an acid solution and determined with Nessler's Reagent. This technique has been used for the analysis of nitrides in lithium and sodium. This method has a lower limit of detection of 2 ppm with a sensitivity of ± 2 ppm. Results have indicated a nitrogen (as nitride) concentration of ≤ 2 ppm in "as produced" cesium, hence additional nitrogen analyses have been discontinued.

Carbon

Carbon is determined by reaction of the alkali metal with water at 0°C , acidification and evaporation to dryness. The carbon is converted to CO_2 by reaction at 600°C with purified oxygen. The CO_2 is measured in a 1 meter cell at 4.4 microns on an infrared spectrometer. The lower limit of this method is 10 ppm with a sensitivity of ± 5 ppm.

Samples of "as-produced" cesium have shown an approximate carbon concentration of 60 ppm. The cesium was hot trapped using zirconium chips (27 gms cesium/gm zirconium) at 1200°F for 16 hours. This procedure reduced the carbon level to 23 ppm. Since this cesium will be used as the supply for the corrosion study, no additional carbon analyses are planned.

Oxygen

Introduction Three techniques of oxygen analysis in cesium have been evaluated.

1. Standard amalgamation extraction of cesium with mercury and determination of residue.

2. Sodium amalgam - extraction of cesium with simultaneously reduction of Cs_2O to Na_2O , and determination of residue.
3. Butyl bromide - reaction of cesium with butyl bromide and determination of unreacted oxide.

The standard amalgamation technique has given consistently low oxygen results. This is attributed to the solubility of cesium oxide in cesium amalgam. To eliminate the solubility problem, it was decided to use a modified amalgamation method where a 0.5 wt% sodium amalgam is used with sodium reducing cesium oxide to sodium oxide which is known to be insoluble in the amalgam. The butyl bromide method has given erratic results. This is attributed to difficulty in purifying reagents although interactions of cesium with the organic reagents may also contribute to the fluctuations which have been observed.

The apparatus which has been used for the study was described in the First Quarterly Progress Report. One modification was made during this report period - the 1 1/2 in. gate valve used as a sampling port began leaking past the seat and this valve was replaced with a 1 1/2 in. ball valve. The ball valve has performed satisfactorily but it has been necessary to replace the seals and rings on one occasion.

Results of Oxygen Analyses - Results are shown in Table 1; this table includes those results which are suspected of contamination but these are appropriately indicated. Runs 38 through 41 were made with the original apparatus. It was during this period that the 1 1/2 in. gate valve developed a leak and results indicated that the samples were being contaminated. Liquid cesium could be found on the valve seat after sitting overnight and the sampling apparatus could not be properly evacuated because of the leak. The system was shut down, the cesium was drained and the vessel washed out. The gate valve was replaced with a 1 1/2 in. ball valve.

The vessel was recharged with cesium and an initial oxygen concentration was established by both the sodium amalgam and the butyl bromide method. The sodium amalgam method showed an average of ~50 ppm O_2 which is in good agreement with previous analyses of "as-produced" cesium. Results found with the butyl bromide method varied to a greater extent than those found with the sodium amalgam method. However, an average of those samples which were known to be free of contamination showed 31 ppm O, approximately

TABLE 1 - ANALYSIS OF CESIUM FOR OXYGEN CONTENT

Sample No.	Sample Weight (Grams)	Oxygen Weight (mg)	O ₂ Concentration (ppm)	Cs ₂ O Concentration (ppm)	Cs in Residue by Titration (mg)	Cs in Residue by Flame (mg)	Na in Residue (mg)	Pot	Temperature (°F)	Anal. Method	Remarks
35	1.84	0.052	28	492	0.87	0.074	0.254	---	---	Na-Hg	O ₂ added 4th time
36	1.91	0.054	122	2150	4.06	0.198	1.13	---	---	Na-Hg	
37	2.01	0.055	124	2180	5.05	0.136	1.26	---	---	Na-Hg	
38	2.46	0.058	247	4360	10.10	0.197	2.21	---	---	Na-Hg	
39	---	0.048	14	---	---	---	---	---	---	Na-Hg	Blank
40	---	0.032	14	---	---	---	---	---	---	Na-Hg	"
41	---	0.024	12	---	---	---	---	---	---	Na-Hg	"
NEW CHARGE AND NEW VALVE											
42	1.96	0.125	64	1126	2.64	0.312	0.681	580	510	Na-Hg	Sample stood overnight - possible leak
43	1.97	0.180	91	1600	2.62	0.481	0.879	580	580	Na-Hg	Possible air leak
44	1.25	0.157	126	2220	3.19	0.448	0.728	580	580	Na-Hg	
45	2.19	0.109	50	880	2.39	0.217	0.579	580	580	Na-Hg	
46	---	---	SAMPLE CONTAMINATED								
47	1.99	0.077	39	681	1.86	0.454	0.470	570	590	Na-Hg	
48	1.46	0.336	202	3555	0.558	---	---	550	550	BB	
49	1.74	0.376	252	4435	0.925	---	---	580	570	BB	
50	1.74	0.048	28	441	0.798	---	---	570	570	BB	
51	1.81	---	---	---	---	---	---	560	480	BB	Sample reacted with BB and stood over weekend
52	1.52	0.028	190	3341	0.479	---	---	560	480	BB	Known contamination - bucket changed color
53	1.675	0.60	38	618	0.825	---	---	570	535	BB	
54	2.14	0.056	37	475	0.930	---	---	580	520	BB	Stood overnight under hexane
55	1.82	0.045	25	434	0.840	---	---	580	520	BB	Stood overnight under hexane - suspected contamination
56	1.53	0.032	21	368	0.532	---	---	580	580	BB	
57	2.16	0.112	52	912	1.46	---	---	580	580	BB	Possible contamination
58	2.23	0.60	27	474	0.996	---	---	600	700	BB	Was under hexane overnight - turned gray
59	---	---	SAMPLE CONTAMINATED								
60	2.40	0.184	60	1300	3.06	0.278	0.747	430	240	Na-Hg	
61	2.25	0.128	81	1000	2.13	0.353	0.505	590	650	Na-Hg	
62	2.52	0.152	52	1184	2.53	0.427	0.708	570	650	Na-Hg	
63	1.85	0.272	147	2590	4.52	0.755	0.930	580	670	Na-Hg	Known contamination
NEW ANALCAM											
64	2.67	0.045	31	552	1.66	0.526	0.424	610	680	Na-Hg	
65	1.64	0.14	21	---	---	0.642	1.45	600	670	Na-Hg	Known contamination
66	2.11	0.015	7	125	0.798	0.710	0.288	600	---	Na-Hg	Hot trapped
67	2.18	0.035	16	22	2.86	0.482	0.298	600	---	Na-Hg	"
68	2.00	0.127	64	1120	---	0.287	0.608	620	---	Na-Hg	"
OXYGEN ADDED TO POT											
69	2.06	0.121	59	1030	2.59	0.511	0.542	610	710	Na-Hg	Sampled 1 hour after O ₂ addition
70	1.94	0.221	114	2010	4.25	0.764	1.08	620	710	Na-Hg	Contaminated black spots
71	1.82	0.248	139	2450	4.78	0.732	1.34	620	740	Na-Hg	Contaminated large black spot
72	---	0.028	---	---	---	---	0.259	---	---	Na-Hg	Blank
73	1.82	0.228	107	1880	3.79	0.705	1.01	630	750	Na-Hg	
74	1.70	0.0	0	0	0.0	---	---	620	750	BB	
75	1.75	0.024	7	123	0.399	---	---	620	750	BB	
76	2.39	0.0	0	0	0.0	---	---	620	750	BB	Same sample lost - obvious error in sample weight
77	2.22	0.304	122	2150	5.05	0.402	1.38	610	720	Na-Hg	
78	2.00	0.204	116	2040	4.39	0.551	1.63	600	700	Na-Hg	
79	---	---	SAMPLE CONTAMINATED								
80	1.91	0.032	17	---	---	---	---	600	700	BB	
81	1.54	0.152	77	1355	2.53	0.761	0.676	610	710	Na-Hg	Dark spot noticed on bucket
82	1.80	0.028	16	---	---	---	---	610	710	BB	
83	2.15	0.10	48	---	---	---	---	620	720	BB	
84	1.97	0.106	53	---	---	---	---	620	720	BB	
85	1.49	0.272	159	2800	4.52	0.394	1.21	600	700	Na-Hg	Small sample weight
86	2.01	0.24	122	---	---	---	---	600	710	BB	
87	1.72	0.11	46	808	1.86	0.279	2.25	600	710	Na-Hg	
88	2.25	0.096	43	---	---	---	---	620	720	BB	
89	1.56	0.16	81	---	---	1.61	3.85	610	720	Na-Hg	
90	2.33	0.084	27	---	---	---	---	610	720	BB	

20 ppm lower than that found with the sodium amalgam method. Of particular interest was Sample #51 which stood over the weekend under butyl bromide and hexane; analysis of this sample showed 0 ppm suggesting that a reaction between the cesium oxide and either butyl bromide or hexane may take place. It is conceivable that lower oxides such as Cs_2O (m.p. -2°C) are metalloid type compounds and might tend to react with butyl bromide.

After the oxygen concentration was established, an equivalent of 300 ppm oxygen was added to the vessel as gaseous oxygen. A sample (No. 69) taken 1 hour after O_2 addition showed 59 ppm oxygen indicating non-equilibrium conditions. Later samples gave results ranging from 114 to 139 ppm O_2 .

Failure to account for all of the oxygen added to the vessel substantiated observations made during earlier additions. To verify that oxygen was not escaping from the cesium during addition, a glass vessel was filled with cesium and a hypodermic needle was immersed to a depth duplicating that used during addition to the test vessel. When oxygen was added to the cesium, a crackling sound could be heard, but there was no visible evidence of oxygen escaping from the cesium surface. Formation of the peroxide or superoxide of cesium would result in low values for oxygen but these compounds would not be expected to form at the concentrations and temperatures (600°F) used in this study. Furthermore, it is assumed that the sodium amalgam procedure would result in the reduction of all oxygen associated with cesium to Na_2O so all oxygen would be recovered. The only plausible explanation for the inability to account for oxygen added to cesium seems to be reduction of cesium oxide by the container material at 600°F .

Samples analysed by the butyl bromide method showed significantly lower results. In one case, a value of 0 ppm was obtained with an apparently valid sample. These results have suggested that the use of the butyl bromide method for analysis of oxygen in cesium be discontinued, within the scope of the present program.

Samples analysed by the sodium amalgam method 2 weeks after oxygen additions showed a decrease from 116 ppm to 46 ppm. This fact is further evidence that the vessel walls are getting oxygen from cesium.

Analyses of hot trapped cesium is represented by Samples Nos. 66, 67 and 68 with known contamination of No. 68. The average of samples 66 and 67 was 11.5 ppm O_2 compared to the typical "as-produced" level of 50 ppm.

A number of runs were made on the sodium amalgam used for cesium extraction to establish a blank or background level. This was done by duplicating the complete procedure of sampling and analysis except that extraction of a cesium sample from the vessel was eliminated. This blank was typically 9 ppm O_2 with a range of 6 to 13 ppm O_2 . Possible sources of this blank were:

1. Incomplete removal of O_2 and/or water from the amalgamation chamber walls.
2. Solubility of Na_2O in sodium amalgam.
3. Occlusion of Na_2O in sodium amalgam.

When the volume of sodium amalgam added to the chamber was varied, the blank varied suggesting that the blank was inherent in the amalgam and not a function of incomplete degassing of the chamber walls. Solubility of Na_2O in the amalgam does not seem to be a valid answer since the oxide would not appear as a residue in the chamber if it were soluble. Occlusion seems to be the most credible answer and variations in the blank level on duplicate samples of the same batch of amalgam seems to verify this. However, this is a preliminary conclusion and additional work is required to elucidate this facet.

Of particular interest to this program is recent work on the analysis of oxygen in potassium performed under MSAR sponsorship. The objective of this study was to determine if the standard amalgamation procedure was valid for potassium analysis. The study was performed in a vessel charged with zirconium chips, and a slow reduction in oxygen level was noted. Samples were analysed by both the standard amalgamation and sodium amalgam methods with the results shown in Table 2. These results indicate that the standard amalgamation method is valid for the analysis of oxygen in potassium. Since the standard amalgamation procedure is less complicated than the MSAR modified procedure, its use is being continued as the method of oxygen analyses of potassium at MSAR.

The application of the sodium amalgam method to the analysis of oxygen in cesium results in more credible data than any other method yet attempted. However, further work is necessary to enable the method to be chosen as a standard technique. This work would include:

1. Quantitative recovery of added oxygen (mass balance).
2. Improvement in blank value precision (or elimination of blank).
3. Effects of oxygen removal by stainless steel vessel walls.

Since the present program is essentially a corrosion program, further work on verification of the method will be discontinued at this time.

TABLE 2 - OXYGEN ANALYSIS OF POTASSIUM

Sample No.	O ₂ Concentration (ppm)	Time at 600°F After Charging (days)	Method
1	29	0	Hg
2	29	0	Hg
3	<u>32</u>	1	Hg
Average	30		
4	17	1	Na-Hg
5	25	1	Na-Hg
6	29	2	Na-Hg
7	24	2	Na-Hg
8	21	3	Na-Hg
9	<u>14</u>	3	Na-Hg
Average	22		
10	17	4	Hg
11	21	5	Hg
12	<u>19</u>	5	Hg
Average	19		

EXPERIMENTAL CORROSION PROGRAM

Table 3 summarizes Haynes-25 capsule tests performed to date. As a control study on the Haynes alloy-25, one capsule (#1) was fabricated and exposed to "as-produced" cesium at 1800°F (982°C) for 104 hours. The capsule showed no extensive corrosion effects (Fig. 3), but increased precipitation at the surface as compared to an air aged specimen (Fig. 2). No attempts was made for a complete analysis of the metals dissolved in cesium.

Photomicrographs (Fig. 3) of samples from the capsule showed 0.4 mil thick zone from the liquid metal interface where grains were affected. Hardness tests on the portions of the capsule exposed to cesium vapor showed the usual age hardening of this alloy ($R_c = 40$) while those in contact with the cesium liquid had no hardness increase over the annealed material ($R_c = 20$). Chemical analyses of a portion of the Haynes-25 capsule exposed to liquid cesium showed a 50 ppm decrease in carbon, a 50 ppm decrease in nitrogen and a 25 ppm increase in oxygen.

Haynes alloy-25 has considerable precipitation during age hardening at test temperatures due to the formation of carbides and intermetallics. Most of this precipitation occurs along grain boundaries and slip planes. When this alloy is exposed to liquid cesium at test temperature, the affected zone (approximately 0.4 mil transverse from the interface) shows a greater degree and more general distribution of precipitates. Near the surface, grain boundaries are most indistinct and there is an increase in grain boundary definition proceeding from the interface into the matrix.

Complete analytical results for capsules exposed 100 hours (#2) and 500 hours (#3) using Haynes alloy-25 with Cb-1%Zr inserts are not yet available for comparison with the control sample. Metallographic examination has shown that both metals used in these tests have a thin coating. X-ray analyses of the Cb-1%Zr inserts have shown these coatings to be CbN. The surface of the Haynes capsules also showed a very thin coating which could have been precipitated on cooling to room temperature. The curved surface is not presently amenable to x-ray diffraction analysis and so this coating has not been analysed. The cesium liquid-vapor interface is easily discernable in capsules 2 and 3 due to the presence of the dark coating in the liquid phase. Contrary to observations on the control sample, hardness in both liquid and vapor zones is $R_c = 36$. The presence of the thin coating is not thought to have any influence on the results of hardness tests which could have possibly given an indication of its composition. The control sample showed a change from age hardened to annealed conditions within a very narrow band (~ 0.1 ") at the cesium liquid-vapor interface.

TABLE 3 - HAYNES-25 CAPSULE TESTS AT 1800°F *

Capsule No.	Tab Insert	Test Duration (hrs)	Hardness of Haynes Surface Exposed to Vapor (R _C)	Hardness of Haynes Surface Exposed to Liquid (R _C)
1	None	104	40	20
2	Cb-1½Zr	100	36	36
3	Cb-1½Zr	500	36	36

* Cs charge = 10 g

The Haynes alloy-25 capsule (#2) which had been exposed for 100 hours at 1800°F (982°C) with a Cb-1%Zr insert in the melt has an affected area averaging 1.4 mils transverse from the surface (Fig. 4). This area is darker than that of the control sample but gives no different appearance under polarized light. The color may be due to a different chemical composition or to variations in chemical etching. The affected zone tapered off at the interface, which was visible through the microscope, but did not reproduce well on a photomicrograph.

The Cb-1%Zr insert from the 100 hour test showed a 1.33% decrease in weight and an average 0.003 in. decrease in thickness. The tab has a 0.4 mil coating of CbN over the entire surface (Fig. 5). A diffusion zone between the CbN coating and the Cb-1%Zr matrix is evident in Figures 5 and 6. Microprobe analyses might verify the composition of this diffusion zone.

The source of the nitrogen for formation of the nitride coating on Cb-1%Zr is hoped to be shown in later analytical results. Previous analysis of cesium has given negligible quantities of nitrogen present in the metal. The nitrogen present in Haynes alloy-25 or traces not completely removed in the argon cover gas seem the only possible sources of nitrogen which had apparently diffused through the cesium. Sufficient nitrogen is probably present in Haynes-25 to cause such a coating.

The Haynes alloy-25 capsule exposed for 500 hours shows physical properties identical to that of the 100 hour test. The transverse affected zone in this test was increased to 2 mils and has the dark appearance of that seen in the 100 hour test. The surface is regular showing no great corrosion but possible solution.

The Cb-1%Zr insert in the 500 hour test experienced no weight loss and no change in thickness as opposed to the 100 hour test which did show significant weight loss. There is a CbN coating which is 0.6 mil thick (Fig. 6). The diffusion zone noted in the 100 hour test is also somewhat larger and more distinct under the microscope.

Test pieces of Mo-0.5%Ti alloy were heated in a controlled atmosphere furnace at 2500°F (1372°C) in an argon atmosphere and in vacuo. The sample tested in argon was kept at temperature for 30 hours in a static argon atmosphere. It gained weight to the amount of 0.2% and experienced an average hardness increase of 6 R_c units. A similar sample exposed 20 hours at temperature in a vacuum of 10 microns mercury experienced no weight loss and no change in hardness. The static argon atmosphere did not eliminate contamination via degassable contaminants in the Mullite, and would probably be improved if a slight flow were used.

The results of these tests indicate that either the argon atmosphere or a vacuum could be used for 2500°F capsule tests. The slight changes encountered with the alloy heated in vacuum seem more favorable for metallographic and chemical analysis and will be employed for the first tests.

One Mo-0.5%Ti capsule has been machined, filled and welded for kinetic solution studies. The presence of the "Lucalox" alumina crucible for sampling at temperature did not significantly hinder any part of the capsule preparation. The Mo-0.5%Ti rod used to suspend the capsule in the furnace is to be welded in the near future. Haynes alloy-25 and Cb-1%Zr capsules for use in the kinetic solution studies of these alloys are also being prepared.

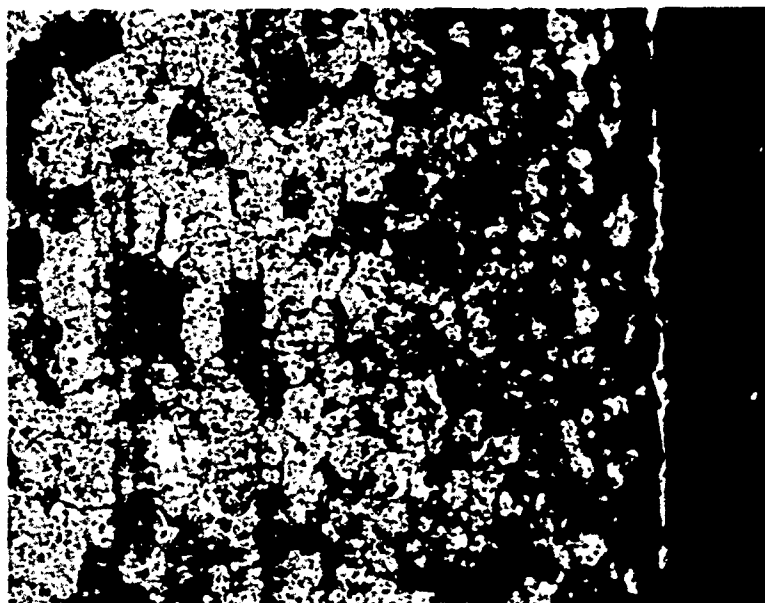


Fig. 5 Nb - 1% Zr Insert from Haynes Capsule
Exposed 100 Hours to Liquid
Cesium
Etchant: $\text{CH}_3\text{CHOHCOOH}$, HNO_3 , HF 266x



Fig. 6 Nb - 1% Zr Insert from Haynes Capsule
Exposed 500 Hours to Liquid
Cesium
Etchant: $\text{CH}_3\text{CHOHCOOH}$, HNO_3 , HF 266x

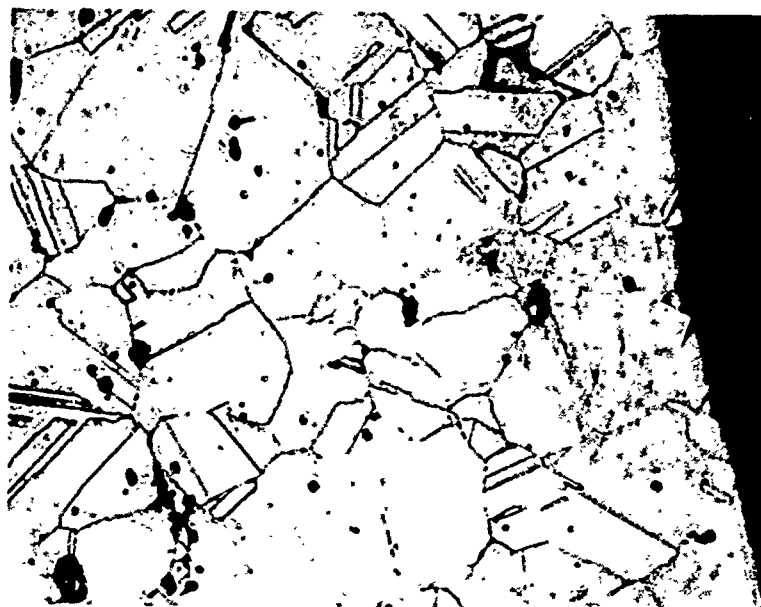
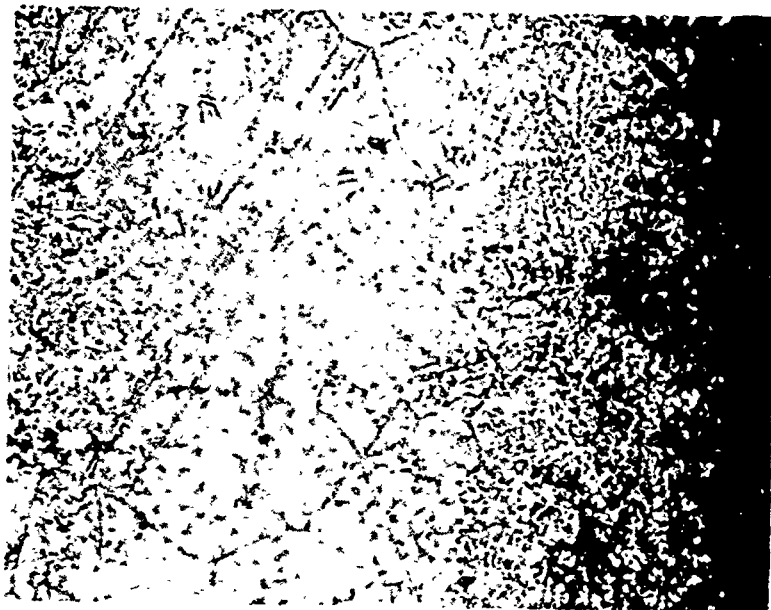


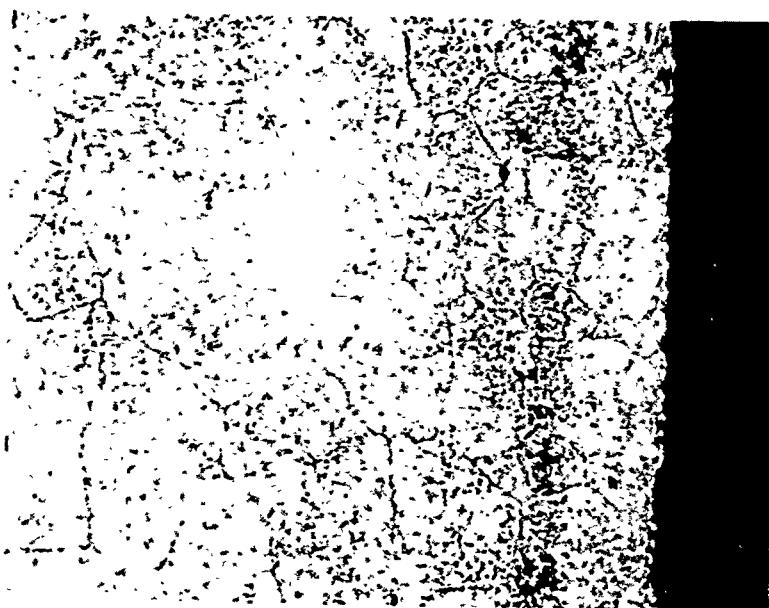
Fig. 1 Haynes Alloy No. 25 "as received"
Etchant: $\text{HCl} - \text{H}_2\text{O}_2$ 266x



Fig. 2 Haynes Alloy Aged 25 Hours in Air
Etchant: $\text{HCl} - \text{H}_2\text{O}_2$ 266x



3 Fig. 3 Haynes Alloy No. 25 Exposed to Liquid Cesium
for 104 Hours
Etchant: $\text{HCl} - \text{H}_2\text{O}_2$ 266x



4 Fig. 4 Haynes Alloy No. 25 Exposed to Liquid
Cesium for 100 Hours with
Nb - 1% Zr Present
Etchant: $\text{HCl} - \text{H}_2\text{O}_2$ 266x